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Table S1 Crystal data and structure refinement for **32**.

Identification code	platon_pl
Empirical formula	C ₁₇ H ₁₄ BrN ₂ O ₃ ReS
Formula weight	592.47
Temperature/K	250(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.6734(5)
b/Å	7.7388(5)
c/Å	17.3622(12)
α /°	83.703(5)
β /°	86.496(6)
γ /°	65.608(5)
Volume/Å ³	933.18(11)
Z	2
ρ_{calc} /cm ³	2.109
μ /mm ⁻¹	8.781
F(000)	560.0
Crystal size/mm ³	0.28 × 0.19 × 0.05
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	2.36 to 50.194
Index ranges	-9 ≤ h ≤ 9, -9 ≤ k ≤ 9, -20 ≤ l ≤ 20
Reflections collected	12031
Independent reflections	3308 [R _{int} = 0.0424, R _{sigma} = 0.0265]
Data/restraints/parameters	3308/0/228
Goodness-of-fit on F ²	1.060
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0237, wR ₂ = 0.0590
Final R indexes [all data]	R ₁ = 0.0269, wR ₂ = 0.0604
Largest diff. peak/hole / e Å ⁻³	1.91/-0.87

Table S2 Bond Lengths for **32**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Re1	Br1	2.6065(6)	N2	C10	1.441(6)
Re1	N1	2.231(4)	C4	C5	1.394(7)
Re1	N2	2.170(4)	C4	C16	1.478(7)
Re1	C1	1.921(5)	C5	C6	1.371(8)
Re1	C2	1.919(5)	C6	C7	1.389(8)
Re1	C3	1.898(5)	C7	C8	1.377(7)
S1	C15	1.766(5)	C8	C9	1.444(6)
S1	C17	1.783(6)	C10	C11	1.380(7)
O1	C1	1.105(6)	C10	C15	1.383(7)
O2	C2	1.150(6)	C11	C12	1.389(8)
O3	C3	1.163(6)	C12	C13	1.369(9)
N1	C4	1.356(6)	C13	C14	1.392(9)
N1	C8	1.362(6)	C14	C15	1.389(7)
N2	C9	1.279(6)			

Table S3 Bond Angles for **32**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Re1	Br1	84.65(9)	O2	C2	Re1	176.7(4)
N2	Re1	Br1	83.87(10)	O3	C3	Re1	178.2(5)
N2	Re1	N1	74.43(13)	N1	C4	C5	120.4(4)
C1	Re1	Br1	175.58(14)	N1	C4	C16	119.9(4)
C1	Re1	N1	92.20(17)	C5	C4	C16	119.7(4)
C1	Re1	N2	98.30(17)	C6	C5	C4	121.2(5)
C2	Re1	Br1	92.02(14)	C5	C6	C7	118.6(5)
C2	Re1	N1	103.87(16)	C8	C7	C6	118.3(5)
C2	Re1	N2	175.66(16)	N1	C8	C7	123.6(4)
C2	Re1	C1	85.71(19)	N1	C8	C9	115.4(4)
C3	Re1	Br1	93.17(16)	C7	C8	C9	121.0(4)
C3	Re1	N1	168.11(17)	N2	C9	C8	119.5(4)
C3	Re1	N2	93.72(17)	C11	C10	N2	117.8(4)
C3	Re1	C1	90.5(2)	C11	C10	C15	121.4(5)
C3	Re1	C2	87.9(2)	C15	C10	N2	120.9(4)
C15	S1	C17	103.3(3)	C10	C11	C12	119.5(6)
C4	N1	Re1	128.4(3)	C13	C12	C11	119.7(6)
C4	N1	C8	117.9(4)	C12	C13	C14	120.8(5)
C8	N1	Re1	113.7(3)	C15	C14	C13	119.8(6)
C9	N2	Re1	116.7(3)	C10	C15	S1	118.0(4)
C9	N2	C10	118.7(4)	C10	C15	C14	118.8(5)
C10	N2	Re1	123.6(3)	C14	C15	S1	123.2(4)
O1	C1	Re1	173.5(4)				

Table S4. Crystal data and structure refinement for **34**.

Identification code	241_in_P-1	
Empirical formula	C17 H14 Br N2 O4 Re S	
Formula weight	608.47	
Temperature	250(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.7208(10) Å	$\alpha = 87.252(10)^\circ$.
	b = 7.8806(10) Å	$\beta = 79.557(10)^\circ$.
	c = 17.915(2) Å	$\gamma = 63.761(9)^\circ$.
Volume	960.9(2) Å ³	
Z	2	
Density (calculated)	2.103 Mg/m ³	
Absorption coefficient	8.535 mm ⁻¹	
F(000)	576	
Crystal size	0.180 x 0.123 x 0.030 mm ³	
Theta range for data collection	2.314 to 25.119°.	
Index ranges	-9 ≤ h ≤ 9, -9 ≤ k ≤ 9, -21 ≤ l ≤ 21	
Reflections collected	12417	
Independent reflections	3415 [R(int) = 0.0331]	
Completeness to theta = 25.119°	99.4 %	
Absorption correction	Integration	
Max. and min. transmission	0.8454 and 0.2787	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3415 / 104 / 237	
Goodness-of-fit on F ²	1.014	
Final R indices [I > 2σ(I)]	R1 = 0.0193, wR2 = 0.0415	
R indices (all data)	R1 = 0.0244, wR2 = 0.0427	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.142 and -0.702 e.Å ⁻³	

Table S5. Bond lengths [\AA] and angles [$^\circ$] for **34**.

C(1)-O(1)	1.146(5)	C(17)-O(4)	1.440(4)
C(1)-Re(1)	1.908(5)	C(17)-H(17A)	0.9700
C(2)-O(2)	1.151(5)	C(17)-H(17B)	0.9700
C(2)-Re(1)	1.898(4)	C(17)-H(17C)	0.9700
C(3)-O(3)	1.139(5)	Br(1)-Re(1)	2.6180(5)
C(3)-Re(1)	1.917(4)	N(1)-Re(1)	2.173(3)
C(4)-C(5)	1.392(6)	N(2)-Re(1)	2.209(3)
C(4)-C(9)	1.395(6)		
C(4)-S(1)	1.749(4)	O(1)-C(1)-Re(1)	178.1(4)
C(5)-C(6)	1.379(7)	O(2)-C(2)-Re(1)	175.8(3)
C(5)-H(5)	0.9400	O(3)-C(3)-Re(1)	179.2(4)
C(6)-C(7)	1.369(8)	C(5)-C(4)-C(9)	117.0(4)
C(6)-H(6)	0.9400	C(5)-C(4)-S(1)	124.0(4)
C(7)-C(8)	1.389(7)	C(9)-C(4)-S(1)	119.0(3)
C(7)-H(7)	0.9400	C(6)-C(5)-C(4)	121.1(5)
C(8)-C(9)	1.370(6)	C(6)-C(5)-H(5)	119.5
C(8)-H(8)	0.9400	C(4)-C(5)-H(5)	119.5
C(9)-N(1)	1.444(5)	C(7)-C(6)-C(5)	120.5(4)
C(10)-N(1)	1.276(5)	C(7)-C(6)-H(6)	119.7
C(10)-C(11)	1.459(5)	C(5)-C(6)-H(6)	119.7
C(10)-H(10)	0.9400	C(6)-C(7)-C(8)	119.8(5)
C(11)-N(2)	1.357(5)	C(6)-C(7)-H(7)	120.1
C(11)-C(12)	1.372(6)	C(8)-C(7)-H(7)	120.1
C(12)-C(13)	1.383(6)	C(9)-C(8)-C(7)	119.2(5)
C(12)-H(12)	0.9400	C(9)-C(8)-H(8)	120.4
C(13)-C(14)	1.365(6)	C(7)-C(8)-H(8)	120.4
C(13)-H(13)	0.9400	C(8)-C(9)-C(4)	122.3(4)
C(14)-C(15)	1.398(5)	C(8)-C(9)-N(1)	117.8(4)
C(14)-H(14)	0.9400	C(4)-C(9)-N(1)	119.9(3)
C(15)-N(2)	1.333(5)	N(1)-C(10)-C(11)	118.8(3)
C(15)-O(4)	1.334(5)	N(1)-C(10)-H(10)	120.6
C(16)-S(1)	1.791(5)	C(11)-C(10)-H(10)	120.6
C(16)-H(16A)	0.9700	N(2)-C(11)-C(12)	123.2(4)
C(16)-H(16B)	0.9700	N(2)-C(11)-C(10)	114.7(3)
C(16)-H(16C)	0.9700	C(12)-C(11)-C(10)	122.1(3)

C(11)-C(12)-C(13)	118.1(4)	C(10)-N(1)-C(9)	118.3(3)
C(11)-C(12)-H(12)	121.0	C(10)-N(1)-Re(1)	116.9(2)
C(13)-C(12)-H(12)	121.0	C(9)-N(1)-Re(1)	123.5(2)
C(14)-C(13)-C(12)	120.0(4)	C(15)-N(2)-C(11)	117.7(3)
C(14)-C(13)-H(13)	120.0	C(15)-N(2)-Re(1)	127.4(2)
C(12)-C(13)-H(13)	120.0	C(11)-N(2)-Re(1)	114.9(2)
C(13)-C(14)-C(15)	118.8(4)	C(15)-O(4)-C(17)	118.8(3)
C(13)-C(14)-H(14)	120.6	C(2)-Re(1)-C(1)	91.49(19)
C(15)-C(14)-H(14)	120.6	C(2)-Re(1)-C(3)	86.85(17)
N(2)-C(15)-O(4)	113.5(3)	C(1)-Re(1)-C(3)	89.28(17)
N(2)-C(15)-C(14)	122.2(3)	C(2)-Re(1)-N(1)	98.81(14)
O(4)-C(15)-C(14)	124.3(3)	C(1)-Re(1)-N(1)	96.07(14)
S(1)-C(16)-H(16A)	109.5	C(3)-Re(1)-N(1)	172.07(15)
S(1)-C(16)-H(16B)	109.5	C(2)-Re(1)-N(2)	92.26(15)
H(16A)-C(16)-H(16B)	109.5	C(1)-Re(1)-N(2)	170.04(14)
S(1)-C(16)-H(16C)	109.5	C(3)-Re(1)-N(2)	100.13(14)
H(16A)-C(16)-H(16C)	109.5	N(1)-Re(1)-N(2)	74.23(11)
H(16B)-C(16)-H(16C)	109.5	C(2)-Re(1)-Br(1)	176.21(12)
O(4)-C(17)-H(17A)	109.5	C(1)-Re(1)-Br(1)	91.78(13)
O(4)-C(17)-H(17B)	109.5	C(3)-Re(1)-Br(1)	91.28(13)
H(17A)-C(17)-H(17B)	109.5	N(1)-Re(1)-Br(1)	82.74(8)
O(4)-C(17)-H(17C)	109.5	N(2)-Re(1)-Br(1)	84.82(8)
H(17A)-C(17)-H(17C)	109.5	C(4)-S(1)-C(16)	103.5(2)
H(17B)-C(17)-H(17C)	109.5		

Symmetry transformations used to generate equivalent atoms:

Table S6. Crystal data and structure refinement for **36**.

Identification code	EK246f	
Empirical formula	C ₂₂ H ₁₅ Br F N ₂ O ₃ Re S	
Formula weight	672.53	
Temperature	250(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 ₁ /n	
Unit cell dimensions	a = 7.9346(4) Å	α = 90°.
	b = 21.9827(11) Å	β = 96.199(4)°.
	c = 12.5942(6) Å	γ = 90°.
Volume	2183.89(19) Å ³	
Z	4	
Density (calculated)	2.045 Mg/m ³	
Absorption coefficient	7.525 mm ⁻¹	
F(000)	1280	
Crystal size	0.310 x 0.253 x 0.210 mm ³	
Theta range for data collection	1.853 to 25.322°.	
Index ranges	-8 ≤ h ≤ 9, -26 ≤ k ≤ 26, -15 ≤ l ≤ 15	
Reflections collected	25356	
Independent reflections	3890 [R(int) = 0.0717]	
Completeness to theta = 25.242°	98.3 %	
Absorption correction	Integration	
Max. and min. transmission	0.1060 and 0.0441	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3890 / 0 / 281	
Goodness-of-fit on F ²	1.089	
Final R indices [I > 2σ(I)]	R1 = 0.0320, wR2 = 0.0732	
R indices (all data)	R1 = 0.0353, wR2 = 0.0763	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.752 and -1.489 e.Å ⁻³	

Table S7. Bond lengths [\AA] and angles [$^\circ$] for **36**.

Re(1)-C(2)	1.905(7)	C(15)-H(15)	0.9300
Re(1)-C(3)	1.915(6)	C(16)-C(17)	1.394(8)
Re(1)-C(1)	1.929(6)	C(16)-C(21)	1.397(8)
Re(1)-N(2)	2.173(4)	C(17)-C(18)	1.387(9)
Re(1)-N(1)	2.227(4)	C(17)-H(17)	0.9300
Re(1)-Br(1)	2.6094(7)	C(18)-C(19)	1.378(10)
S(1)-C(21)	1.768(6)	C(18)-H(18)	0.9300
S(1)-C(22)	1.794(6)	C(19)-C(20)	1.366(10)
F(1)-C(6)	1.363(7)	C(19)-H(19)	0.9300
O(1)-C(1)	1.145(7)	C(20)-C(21)	1.396(8)
O(2)-C(2)	1.149(8)	C(20)-H(20)	0.9300
O(3)-C(3)	1.146(7)	C(22)-H(22A)	0.9600
N(1)-C(10)	1.344(6)	C(22)-H(22B)	0.9600
N(1)-C(14)	1.355(7)	C(22)-H(22C)	0.9600
N(2)-C(15)	1.279(7)		
N(2)-C(16)	1.443(7)	C(2)-Re(1)-C(3)	88.4(2)
C(4)-C(9)	1.381(8)	C(2)-Re(1)-C(1)	89.9(2)
C(4)-C(5)	1.388(8)	C(3)-Re(1)-C(1)	86.0(2)
C(4)-H(4)	0.9300	C(2)-Re(1)-N(2)	95.6(2)
C(5)-C(6)	1.381(10)	C(3)-Re(1)-N(2)	96.5(2)
C(5)-H(5)	0.9300	C(1)-Re(1)-N(2)	174.0(2)
C(6)-C(7)	1.349(10)	C(2)-Re(1)-N(1)	95.0(2)
C(7)-C(8)	1.394(8)	C(3)-Re(1)-N(1)	170.95(19)
C(7)-H(7)	0.9300	C(1)-Re(1)-N(1)	102.3(2)
C(8)-C(9)	1.386(8)	N(2)-Re(1)-N(1)	74.80(16)
C(8)-H(8)	0.9300	C(2)-Re(1)-Br(1)	176.33(18)
C(9)-C(10)	1.486(7)	C(3)-Re(1)-Br(1)	95.25(17)
C(10)-C(11)	1.388(8)	C(1)-Re(1)-Br(1)	90.23(18)
C(11)-C(12)	1.368(8)	N(2)-Re(1)-Br(1)	84.15(12)
C(11)-H(11)	0.9300	N(1)-Re(1)-Br(1)	81.42(11)
C(12)-C(13)	1.373(8)	C(21)-S(1)-C(22)	103.5(3)
C(12)-H(12)	0.9300	C(10)-N(1)-C(14)	117.6(4)
C(13)-C(14)	1.389(8)	C(10)-N(1)-Re(1)	128.5(3)
C(13)-H(13)	0.9300	C(14)-N(1)-Re(1)	113.2(3)
C(14)-C(15)	1.451(7)	C(15)-N(2)-C(16)	118.9(4)

C(15)-N(2)-Re(1)	116.2(3)	C(12)-C(13)-H(13)	120.9
C(16)-N(2)-Re(1)	124.7(3)	C(14)-C(13)-H(13)	120.9
O(1)-C(1)-Re(1)	175.8(5)	N(1)-C(14)-C(13)	123.6(5)
O(2)-C(2)-Re(1)	178.7(5)	N(1)-C(14)-C(15)	115.8(5)
O(3)-C(3)-Re(1)	179.5(5)	C(13)-C(14)-C(15)	120.5(5)
C(9)-C(4)-C(5)	121.6(6)	N(2)-C(15)-C(14)	119.4(5)
C(9)-C(4)-H(4)	119.2	N(2)-C(15)-H(15)	120.3
C(5)-C(4)-H(4)	119.2	C(14)-C(15)-H(15)	120.3
C(6)-C(5)-C(4)	116.6(6)	C(17)-C(16)-C(21)	120.6(5)
C(6)-C(5)-H(5)	121.7	C(17)-C(16)-N(2)	117.7(5)
C(4)-C(5)-H(5)	121.7	C(21)-C(16)-N(2)	121.6(5)
C(7)-C(6)-F(1)	118.4(6)	C(18)-C(17)-C(16)	120.1(6)
C(7)-C(6)-C(5)	124.2(6)	C(18)-C(17)-H(17)	120.0
F(1)-C(6)-C(5)	117.3(7)	C(16)-C(17)-H(17)	120.0
C(6)-C(7)-C(8)	118.0(6)	C(19)-C(18)-C(17)	119.1(6)
C(6)-C(7)-H(7)	121.0	C(19)-C(18)-H(18)	120.4
C(8)-C(7)-H(7)	121.0	C(17)-C(18)-H(18)	120.4
C(9)-C(8)-C(7)	120.4(6)	C(20)-C(19)-C(18)	121.1(6)
C(9)-C(8)-H(8)	119.8	C(20)-C(19)-H(19)	119.4
C(7)-C(8)-H(8)	119.8	C(18)-C(19)-H(19)	119.4
C(4)-C(9)-C(8)	119.1(5)	C(19)-C(20)-C(21)	121.1(6)
C(4)-C(9)-C(10)	120.2(5)	C(19)-C(20)-H(20)	119.4
C(8)-C(9)-C(10)	120.2(5)	C(21)-C(20)-H(20)	119.4
N(1)-C(10)-C(11)	120.7(5)	C(20)-C(21)-C(16)	117.9(6)
N(1)-C(10)-C(9)	120.2(5)	C(20)-C(21)-S(1)	123.6(5)
C(11)-C(10)-C(9)	119.0(5)	C(16)-C(21)-S(1)	118.5(4)
C(12)-C(11)-C(10)	121.5(5)	S(1)-C(22)-H(22A)	109.5
C(12)-C(11)-H(11)	119.2	S(1)-C(22)-H(22B)	109.5
C(10)-C(11)-H(11)	119.2	H(22A)-C(22)-H(22B)	109.5
C(11)-C(12)-C(13)	118.4(5)	S(1)-C(22)-H(22C)	109.5
C(11)-C(12)-H(12)	120.8	H(22A)-C(22)-H(22C)	109.5
C(13)-C(12)-H(12)	120.8	H(22B)-C(22)-H(22C)	109.5
C(12)-C(13)-C(14)	118.2(5)		

Symmetry transformations used to generate equivalent atoms:

Table S8. Crystal data and structure refinement for **38**.

Identification code	shelx	
Empirical formula	C ₂₀ H ₁₄ Br N ₂ O ₃ Re S	
Formula weight	628.50	
Temperature	250(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 ₁ /n	
Unit cell dimensions	a = 10.0632(4) Å	α = 90°.
	b = 11.6027(3) Å	β = 99.629(4)°.
	c = 17.3107(8) Å	γ = 90°.
Volume	1992.73(13) Å ³	
Z	4	
Density (calculated)	2.095 Mg/m ³	
Absorption coefficient	8.231 mm ⁻¹	
F(000)	1192	
Crystal size	0.440 x 0.220 x 0.070 mm ³	
Theta range for data collection	2.122 to 25.080°.	
Index ranges	-11 ≤ h ≤ 12, -12 ≤ k ≤ 13, -20 ≤ l ≤ 20	
Reflections collected	25006	
Independent reflections	3524 [R(int) = 0.0411]	
Completeness to theta = 25.080°	99.9 %	
Absorption correction	Integration	
Max. and min. transmission	0.6113 and 0.2293	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3524 / 0 / 265	
Goodness-of-fit on F ²	1.037	
Final R indices [I > 2σ(I)]	R1 = 0.0219, wR2 = 0.0500	
R indices (all data)	R1 = 0.0256, wR2 = 0.0515	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.612 and -0.809 e.Å ⁻³	

Table S9. Bond lengths [\AA] and angles [$^\circ$] for **38**.

C(1)-O(1)	1.153(6)	C(18)-C(19)	1.400(7)
C(1)-Re(1)	1.904(5)	C(18)-H(18)	0.9400
C(2)-O(2)	1.157(5)	C(19)-S(1)	1.763(5)
C(2)-Re(1)	1.906(5)	C(20A)-S(1)	1.804(11)
C(3)-O(3)	1.156(5)	C(20A)-H(20A)	0.9700
C(3)-Re(1)	1.908(5)	C(20A)-H(20B)	0.9700
C(4)-N(1)	1.377(5)	C(20A)-H(20C)	0.9700
C(4)-C(5)	1.417(6)	C(20B)-S(1)	1.72(3)
C(4)-C(9)	1.418(6)	C(20B)-H(20D)	0.9700
C(5)-C(6)	1.364(6)	C(20B)-H(20E)	0.9700
C(5)-H(5)	0.9400	C(20B)-H(20F)	0.9700
C(6)-C(7)	1.399(7)	Br(1)-Re(1)	2.6133(5)
C(6)-H(6)	0.9400	N(1)-Re(1)	2.225(3)
C(7)-C(8)	1.356(7)	N(2)-Re(1)	2.189(3)
C(7)-H(7)	0.9400		
C(8)-C(9)	1.412(6)	O(1)-C(1)-Re(1)	176.7(4)
C(8)-H(8)	0.9400	O(2)-C(2)-Re(1)	176.0(4)
C(9)-C(10)	1.405(6)	O(3)-C(3)-Re(1)	177.0(4)
C(10)-C(11)	1.361(6)	N(1)-C(4)-C(5)	120.2(4)
C(10)-H(10)	0.9400	N(1)-C(4)-C(9)	121.6(4)
C(11)-C(12)	1.393(6)	C(5)-C(4)-C(9)	118.2(4)
C(11)-H(11)	0.9400	C(6)-C(5)-C(4)	120.4(4)
C(12)-N(1)	1.346(5)	C(6)-C(5)-H(5)	119.8
C(12)-C(13)	1.458(6)	C(4)-C(5)-H(5)	119.8
C(13)-N(2)	1.272(5)	C(5)-C(6)-C(7)	121.0(4)
C(13)-H(13)	0.9400	C(5)-C(6)-H(6)	119.5
C(14)-C(19)	1.388(6)	C(7)-C(6)-H(6)	119.5
C(14)-C(15)	1.390(7)	C(8)-C(7)-C(6)	120.3(4)
C(14)-N(2)	1.449(5)	C(8)-C(7)-H(7)	119.9
C(15)-C(16)	1.373(7)	C(6)-C(7)-H(7)	119.9
C(15)-H(15)	0.9400	C(7)-C(8)-C(9)	120.5(4)
C(16)-C(17)	1.375(8)	C(7)-C(8)-H(8)	119.7
C(16)-H(16)	0.9400	C(9)-C(8)-H(8)	119.7
C(17)-C(18)	1.373(8)	C(10)-C(9)-C(8)	122.2(4)
C(17)-H(17)	0.9400	C(10)-C(9)-C(4)	118.2(4)

C(8)-C(9)-C(4)	119.6(4)	H(20A)-C(20A)-H(20B)	109.5
C(11)-C(10)-C(9)	119.9(4)	S(1)-C(20A)-H(20C)	109.5
C(11)-C(10)-H(10)	120.1	H(20A)-C(20A)-H(20C)	109.5
C(9)-C(10)-H(10)	120.1	H(20B)-C(20A)-H(20C)	109.5
C(10)-C(11)-C(12)	119.0(4)	S(1)-C(20B)-H(20D)	109.5
C(10)-C(11)-H(11)	120.5	S(1)-C(20B)-H(20E)	109.5
C(12)-C(11)-H(11)	120.5	H(20D)-C(20B)-H(20E)	109.5
N(1)-C(12)-C(11)	123.9(4)	S(1)-C(20B)-H(20F)	109.5
N(1)-C(12)-C(13)	115.7(4)	H(20D)-C(20B)-H(20F)	109.5
C(11)-C(12)-C(13)	120.3(4)	H(20E)-C(20B)-H(20F)	109.5
N(2)-C(13)-C(12)	119.6(4)	C(12)-N(1)-C(4)	117.3(3)
N(2)-C(13)-H(13)	120.2	C(12)-N(1)-Re(1)	113.4(3)
C(12)-C(13)-H(13)	120.2	C(4)-N(1)-Re(1)	129.3(2)
C(19)-C(14)-C(15)	120.7(4)	C(13)-N(2)-C(14)	117.4(3)
C(19)-C(14)-N(2)	121.3(4)	C(13)-N(2)-Re(1)	115.2(3)
C(15)-C(14)-N(2)	118.0(4)	C(14)-N(2)-Re(1)	125.4(2)
C(16)-C(15)-C(14)	120.3(5)	C(1)-Re(1)-C(2)	87.41(19)
C(16)-C(15)-H(15)	119.9	C(1)-Re(1)-C(3)	89.18(18)
C(14)-C(15)-H(15)	119.9	C(2)-Re(1)-C(3)	84.74(17)
C(15)-C(16)-C(17)	119.6(5)	C(1)-Re(1)-N(2)	99.55(15)
C(15)-C(16)-H(16)	120.2	C(2)-Re(1)-N(2)	97.62(15)
C(17)-C(16)-H(16)	120.2	C(3)-Re(1)-N(2)	171.04(15)
C(18)-C(17)-C(16)	120.7(5)	C(1)-Re(1)-N(1)	92.53(16)
C(18)-C(17)-H(17)	119.6	C(2)-Re(1)-N(1)	172.00(15)
C(16)-C(17)-H(17)	119.6	C(3)-Re(1)-N(1)	103.26(15)
C(17)-C(18)-C(19)	120.7(5)	N(2)-Re(1)-N(1)	74.49(12)
C(17)-C(18)-H(18)	119.7	C(1)-Re(1)-Br(1)	176.69(15)
C(19)-C(18)-H(18)	119.7	C(2)-Re(1)-Br(1)	94.67(14)
C(14)-C(19)-C(18)	118.0(5)	C(3)-Re(1)-Br(1)	88.45(13)
C(14)-C(19)-S(1)	118.6(4)	N(2)-Re(1)-Br(1)	82.75(9)
C(18)-C(19)-S(1)	123.1(4)	N(1)-Re(1)-Br(1)	85.77(8)
S(1)-C(20A)-H(20A)	109.5	C(20B)-S(1)-C(19)	112.9(11)
S(1)-C(20A)-H(20B)	109.5	C(19)-S(1)-C(20A)	99.7(4)

Table S10. Crystal data and structure refinement for **44**.

Identification code	232s_SQUEEZE	
Empirical formula	C ₂₄ H ₁₂ Br ₂ N ₄ O ₆ Re ₂	
Formula weight	984.60	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 17.6909(8) Å	$\alpha = 90^\circ$.
	b = 24.7765(7) Å	$\beta = 99.689(4)^\circ$.
	c = 6.8265(2) Å	$\gamma = 90^\circ$.
Volume	2949.50(18) Å ³	
Z	4	
Density (calculated)	2.217 Mg/m ³	
Absorption coefficient	10.952 mm ⁻¹	
F(000)	1808	
Crystal size	0.250 x 0.117 x 0.050 mm ³	
Theta range for data collection	1.428 to 25.159°.	
Index ranges	-21 ≤ h ≤ 21, -29 ≤ k ≤ 29, -8 ≤ l ≤ 8	
Reflections collected	18886	
Independent reflections	2624 [R(int) = 0.0457]	
Completeness to theta = 25.159°	99.1 %	
Absorption correction	Integration	
Max. and min. transmission	0.0798 and 0.0473	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2624 / 9 / 172	
Goodness-of-fit on F ²	1.073	
Final R indices [I > 2σ(I)]	R1 = 0.0419, wR2 = 0.1266	
R indices (all data)	R1 = 0.0468, wR2 = 0.1309	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.781 and -1.982 e.Å ⁻³	

Table S11. Bond lengths [Å] and angles [°] for **44**.

C(1)-O(1)	1.158(12)	C(5)-C(4)-H(4)	118.9
C(1)-Re(1)	1.904(10)	C(4)-C(5)-C(6)	119.5(9)
C(2)-O(2)	1.157(13)	C(4)-C(5)-H(5)	120.2
C(2)-Re(1)	1.927(13)	C(6)-C(5)-H(5)	120.2
C(3)-O(3)	1.131(11)	C(5)-C(6)-C(7)	118.8(9)
C(3)-Re(1)	1.939(10)	C(5)-C(6)-H(6)	120.6
C(4)-N(1)	1.334(12)	C(7)-C(6)-H(6)	120.6
C(4)-C(5)	1.378(13)	C(8)-C(7)-C(6)	118.2(9)
C(4)-H(4)	0.9300	C(8)-C(7)-H(7)	120.9
C(5)-C(6)	1.380(15)	C(6)-C(7)-H(7)	120.9
C(5)-H(5)	0.9300	N(1)-C(8)-C(7)	123.3(8)
C(6)-C(7)	1.384(14)	N(1)-C(8)-C(9)	113.9(8)
C(6)-H(6)	0.9300	C(7)-C(8)-C(9)	122.3(8)
C(7)-C(8)	1.370(12)	N(2)-C(9)-C(9)#1	121.5(6)
C(7)-H(7)	0.9300	N(2)-C(9)-C(8)	115.6(8)
C(8)-N(1)	1.354(12)	C(9)#1-C(9)-C(8)	122.7(6)
C(8)-C(9)	1.492(12)	N(2)-C(10)-C(10)#1	120.9(5)
C(9)-N(2)	1.345(12)	N(2)-C(10)-C(11)	119.3(9)
C(9)-C(9)#1	1.391(19)	C(10)#1-C(10)-C(11)	119.4(6)
C(10)-N(2)	1.392(12)	C(12)-C(11)-C(10)	120.0(11)
C(10)-C(10)#1	1.40(2)	C(12)-C(11)-H(11)	120.0
C(10)-C(11)	1.419(13)	C(10)-C(11)-H(11)	120.0
C(11)-C(12)	1.349(14)	C(11)-C(12)-C(12)#1	120.6(7)
C(11)-H(11)	0.9300	C(11)-C(12)-H(12)	119.7
C(12)-C(12)#1	1.42(2)	C(12)#1-C(12)-H(12)	119.7
C(12)-H(12)	0.9300	C(4)-N(1)-C(8)	117.6(8)
Br(1)-Re(1)	2.6085(11)	C(4)-N(1)-Re(1)	126.2(7)
N(1)-Re(1)	2.156(7)	C(8)-N(1)-Re(1)	116.2(6)
N(2)-Re(1)	2.209(8)	C(9)-N(2)-C(10)	115.8(8)
		C(9)-N(2)-Re(1)	110.8(6)
O(1)-C(1)-Re(1)	178.9(8)	C(10)-N(2)-Re(1)	131.4(6)
O(2)-C(2)-Re(1)	173.2(9)	C(1)-Re(1)-C(2)	86.9(4)
O(3)-C(3)-Re(1)	178.1(8)	C(1)-Re(1)-C(3)	90.0(4)
N(1)-C(4)-C(5)	122.3(9)	C(2)-Re(1)-C(3)	87.2(4)
N(1)-C(4)-H(4)	118.9	C(1)-Re(1)-N(1)	96.3(3)

C(2)-Re(1)-N(1)	95.7(4)	C(1)-Re(1)-Br(1)	176.1(4)
C(3)-Re(1)-N(1)	173.2(3)	C(2)-Re(1)-Br(1)	96.9(3)
C(1)-Re(1)-N(2)	95.2(4)	C(3)-Re(1)-Br(1)	89.9(3)
C(2)-Re(1)-N(2)	171.0(3)	N(1)-Re(1)-Br(1)	83.66(19)
C(3)-Re(1)-N(2)	101.6(4)	N(2)-Re(1)-Br(1)	81.03(18)
N(1)-Re(1)-N(2)	75.3(3)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+1/2

Table S12 Crystal data and structure refinement for **46**.

Identification code	EK258s
Empirical formula	C ₁₄ H ₆ BrN ₂ O ₄ Re
Formula weight	532.32
Temperature/K	250
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	6.5444(7)
b/Å	16.7778(15)
c/Å	13.2362(13)
α /°	90
β /°	100.107(8)
γ /°	90
Volume/Å ³	1430.8(2)
Z	4
ρ_{calc} /cm ³	2.471
μ /mm ⁻¹	11.304
F(000)	984.0
Crystal size/mm ³	0.34 × 0.14 × 0.02
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	3.958 to 51.434
Index ranges	-7 ≤ h ≤ 7, -20 ≤ k ≤ 20, -15 ≤ l ≤ 15
Reflections collected	29903
Independent reflections	29903 [R _{int} = ?, R _{sigma} = 0.0797]
Data/restraints/parameters	29903/4/177
Goodness-of-fit on F ²	1.290
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.1350, wR ₂ = 0.3407
Final R indexes [all data]	R ₁ = 0.2117, wR ₂ = 0.4086
Largest diff. peak/hole / e Å ⁻³	5.51/-3.48

Table S13 Bond Lengths for **46**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Re1	Br1	2.570(9)	C5	C7	1.27(2)
Re1	N1	2.237(18)	C4	C3	1.3900
Re1	N2	2.286(16)	C4	C6	1.52(3)
Re1	C12	1.86(5)	C3	C2	1.3900
Re1	C13	1.83(4)	C2	C1	1.3900
Re1	C14	1.88(4)	C6	C8	1.52(3)
O1	C6	1.23(4)	C9	C8	1.3900
O2	C12	1.21(5)	C9	C10	1.3900
O3	C13	1.23(5)	C8	C7	1.3900
O4	C14	1.10(3)	C7	N2	1.3900
N1	C5	1.3900	N2	C11	1.3900
N1	C1	1.3900	C11	C10	1.3900
C5	C4	1.3900			

Table S14 Bond Angles for **46**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Re1	Br1	86.1(8)	C3	C4	C6	137.3(19)
N1	Re1	N2	79.1(7)	C2	C3	C4	120.0
N2	Re1	Br1	85.6(8)	C1	C2	C3	120.0
C12	Re1	Br1	90.9(16)	C2	C1	N1	120.0
C12	Re1	N1	95.5(14)	O1	C6	C4	126(3)
C12	Re1	N2	173.8(14)	O1	C6	C8	128(3)
C12	Re1	C14	89.8(19)	C4	C6	C8	106(2)
C13	Re1	Br1	96.7(17)	C8	C9	C10	120.0
C13	Re1	N1	174.4(18)	C9	C8	C6	138(2)
C13	Re1	N2	96.3(15)	C9	C8	C7	120.0
C13	Re1	C12	89(2)	C7	C8	C6	102.2(19)
C13	Re1	C14	91(2)	C5	C7	C8	114.8(19)
C14	Re1	Br1	172.2(13)	C5	C7	N2	125.1(19)
C14	Re1	N1	86.0(15)	N2	C7	C8	120.0
C14	Re1	N2	93.0(13)	C7	N2	Re1	104.4(12)
C5	N1	Re1	105.6(11)	C7	N2	C11	120.0
C5	N1	C1	120.0	C11	N2	Re1	135.5(12)
C1	N1	Re1	134.3(11)	N2	C11	C10	120.0
C4	C5	N1	120.0	C11	C10	C9	120.0
C7	C5	N1	125.7(18)	O2	C12	Re1	177(4)
C7	C5	C4	114.3(18)	O3	C13	Re1	176(5)
C5	C4	C3	120.0	O4	C14	Re1	178(3)
C5	C4	C6	102.6(18)				

Table S15 Crystal data and structure refinement for **49**.

Identification code	E-249-B2
Empirical formula	C ₁₅ H ₁₂ BrMnN ₂ O ₄
Formula weight	419.12
Temperature/K	250
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	9.0940(5)
b/Å	15.1304(9)
c/Å	11.5589(7)
α /°	90
β /°	99.670(5)
γ /°	90
Volume/Å ³	1567.86(16)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.776
μ/mm^{-1}	3.411
F(000)	832.0
Crystal size/mm ³	0.22 × 0.17 × 0.13
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	4.474 to 53.788
Index ranges	-11 ≤ h ≤ 11, -19 ≤ k ≤ 19, -14 ≤ l ≤ 14
Reflections collected	21140
Independent reflections	3352 [R_{int} = 0.0631, R_{sigma} = 0.0322]
Data/restraints/parameters	3352/0/211
Goodness-of-fit on F ²	1.095
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0397, wR_2 = 0.0982
Final R indexes [all data]	R_1 = 0.0587, wR_2 = 0.1093
Largest diff. peak/hole / e Å ⁻³	0.55/-0.51

Table S16 Bond Lengths for **49**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Mn1	2.5310(6)	N2	C6	1.364(4)
Mn1	N1	2.042(3)	N2	C10	1.350(5)
Mn1	N2	2.099(3)	C1	C2	1.375(6)
Mn1	C13	1.786(4)	C2	C3	1.371(6)
Mn1	C14	1.801(4)	C3	C4	1.372(6)
Mn1	C15	1.805(4)	C4	C5	1.391(5)
O1	C8	1.348(4)	C5	C6	1.473(5)
O1	C12	1.432(5)	C6	C7	1.372(5)
O2	C13	1.161(5)	C7	C8	1.381(5)
O3	C14	1.141(5)	C8	C9	1.377(5)
O4	C15	1.128(4)	C9	C10	1.391(5)
N1	C1	1.347(5)	C10	C11	1.495(5)
N1	C5	1.344(4)			

Table S17 Bond Angles for **49**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Mn1	Br1	86.95(8)	N1	C1	C2	122.3(4)
N1	Mn1	N2	78.97(11)	C3	C2	C1	119.0(4)
N2	Mn1	Br1	87.50(8)	C2	C3	C4	119.3(4)
C13	Mn1	Br1	91.54(12)	C3	C4	C5	119.4(4)
C13	Mn1	N1	94.43(15)	N1	C5	C4	121.2(3)
C13	Mn1	N2	173.37(15)	N1	C5	C6	115.3(3)
C13	Mn1	C14	84.10(18)	C4	C5	C6	123.5(3)
C13	Mn1	C15	91.40(16)	N2	C6	C5	115.4(3)
C14	Mn1	Br1	85.54(12)	N2	C6	C7	122.9(3)
C14	Mn1	N1	172.31(15)	C7	C6	C5	121.7(3)
C14	Mn1	N2	102.35(16)	C6	C7	C8	119.6(3)
C14	Mn1	C15	92.63(16)	O1	C8	C7	116.3(3)
C15	Mn1	Br1	176.35(12)	O1	C8	C9	125.2(4)
C15	Mn1	N1	94.96(14)	C9	C8	C7	118.4(3)
C15	Mn1	N2	89.82(14)	C8	C9	C10	119.6(4)
C8	O1	C12	117.8(3)	N2	C10	C9	122.4(3)
C1	N1	Mn1	124.9(3)	N2	C10	C11	119.6(3)
C5	N1	Mn1	116.0(2)	C9	C10	C11	117.9(4)
C5	N1	C1	118.6(3)	O2	C13	Mn1	176.6(4)
C6	N2	Mn1	113.5(2)	O3	C14	Mn1	172.7(4)
C10	N2	Mn1	129.5(2)	O4	C15	Mn1	178.9(3)
C10	N2	C6	117.0(3)				

Table S18 Crystal data and structure refinement for **50**.

Identification code	E250-Re
Empirical formula	C ₁₅ H ₁₂ BrN ₂ O ₄ Re
Formula weight	550.38
Temperature/K	250(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.9055(10)
b/Å	8.3868(10)
c/Å	12.1769(14)
α /°	93.574(9)
β /°	93.489(10)
γ /°	90.658(10)
Volume/Å ³	804.19(17)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	2.273
μ/mm^{-1}	10.060
F(000)	516.0
Crystal size/mm ³	0.21 × 0.1 × 0.07
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	3.358 to 54.432
Index ranges	-10 ≤ h ≤ 10, -10 ≤ k ≤ 10, -15 ≤ l ≤ 15
Reflections collected	34541
Independent reflections	34541 [R_{int} = ?, R_{sigma} = 0.0470]
Data/restraints/parameters	34541/3/188
Goodness-of-fit on F ²	1.073
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0793, wR_2 = 0.2254
Final R indexes [all data]	R_1 = 0.1143, wR_2 = 0.2600
Largest diff. peak/hole / e Å ⁻³	2.50/-2.18

Table S19 Bond Lengths for **50**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Re1	Br1	2.623(2)	C1	C2	1.3900
Re1	N1	2.157(7)	C2	C3	1.3900
Re1	N2	2.223(7)	C3	C4	1.3900
Re1	C13	2.01(2)	C4	C5	1.3900
Re1	C14	1.92(2)	C5	C6	1.419(10)
Re1	C15	1.91(2)	C6	C7	1.3900
O1	C8	1.335(16)	C6	N2	1.3900
O1	C12	1.41(3)	C7	C8	1.3900
O2	C13	1.04(3)	C8	C9	1.3900
O3	C14	1.15(2)	C9	C10	1.3900
O4	C15	1.14(3)	C10	N2	1.3900
N1	C1	1.3900	C10	C11	1.46(2)
N1	C5	1.3900			

Table S20 Bond Angles for **50**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Re1	Br1	85.1(3)	C5	C4	C3	120.0
N1	Re1	N2	75.0(4)	N1	C5	C6	114.6(7)
N2	Re1	Br1	84.1(3)	C4	C5	N1	120.0
C13	Re1	Br1	176.2(5)	C4	C5	C6	125.3(7)
C13	Re1	N1	92.9(6)	C7	C6	C5	120.6(7)
C13	Re1	N2	92.2(6)	C7	C6	N2	120.0
C14	Re1	Br1	90.1(7)	N2	C6	C5	118.8(7)
C14	Re1	N1	175.2(7)	C6	C7	C8	120.0
C14	Re1	N2	105.0(7)	O1	C8	C7	115.9(10)
C14	Re1	C13	91.9(8)	O1	C8	C9	123.9(10)
C15	Re1	Br1	92.3(7)	C7	C8	C9	120.0
C15	Re1	N1	95.9(7)	C10	C9	C8	120.0
C15	Re1	N2	170.4(7)	C9	C10	N2	120.0
C15	Re1	C13	91.1(9)	C9	C10	C11	121.2(11)
C15	Re1	C14	83.8(9)	N2	C10	C11	118.8(11)
C8	O1	C12	119.7(16)	C6	N2	Re1	112.7(5)
C1	N1	Re1	122.6(5)	C10	N2	Re1	127.3(5)
C1	N1	C5	120.0	C10	N2	C6	120.0
C5	N1	Re1	117.2(5)	O2	C13	Re1	177.4(17)
C2	C1	N1	120.0	O3	C14	Re1	175.2(19)
C1	C2	C3	120.0	O4	C15	Re1	179(2)
C2	C3	C4	120.0				